Report on PDF Models for Turbulence Chemistry Interaction

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Abstract

Many numerical solvers aimed at the solution of high speed chemically reacting flows employ methods that solve directly for both the change in thermal and mass diffusivity due to turbulence through the solution of a turbulent Prandtl and turbulent Schmidt number directly. In many cases, the solution of the turbulent Schmidt number requires a method of modelling the effects of species massfraction fluctuations on the source terms representing the chemical reactions occurring. One approach that has seen reasonable success is the use of Probability Density Functions (PDFs) to evaluate the time averaged values of fluctuating massfraction terms appearing in the governing equations. Both assumed forms for these PDFs as well as PDFs where their evolution itself is part of the solution procedure have been implemented. The assumed forms have generally been regarded as being the best combination of accuracy and computational efficiency. Indeed, the use of a multivariate β PDF for the species massfraction fluctuations reduces to an algebraic expression avoiding the need to numerically integrate the PDF (as is required when using a Gaussian PDF). This report details the implementation of assumed, jointly un-correlated PDFs for both temperature and species massfraction fluctuations. It shows that provided one is already using a variable Prandtl and/or variable Schmidt number numerical solver, no additional conservation equations are required (the use of a temperature PDF requires the variable Prandtl number solver, the use of a composition PDF requires the variable Schmidt number solver).

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Executive summary

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This report describes the use of Probability Density Functions (PDFs) in the calculation of turbulent, chemically reacting flowfields. The requirement for the modelling of chemical source terms is reviewed through the development of the Favre averaged species conservation equation. The relationship between a time averaged and expected, or mean, value (which can be found using a PDF) is then presented. This is followed by the derivation of the chemical source term to highlight the manner in which PDFs can be used to solve for this term while considering fluctuations in species massfractions.

The use of marginal, or jointly un-correlated, PDFs is presented using a clipped, Gaussian PDF for the fluctuations in temperature and a multivariate β PDF for species massfraction fluctuations. It is shown how the use of the multivariate β PDF reduces to the solution of a set of algebraic equations eliminating the need to numerically integrate the PDF. This algebraic expression requires the solution of the time averaged species massfraction and the sum of the species massfraction variance, where the variance is assumed known (this is often solved for as part of a variable Schmidt number numerical solver).

The report also contains a brief review of relevant papers utilizing the methods described in this work and concludes with some recommendations for future work.

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1 Introduction

The determination of fluctuating components within a turbulent flowfield has long been an area of significant computational research given the ease with which laminar values, or time averaged values, can be calculated using reasonably efficient Navier-Stokes solvers. This has led to a wide variety of turbulence models whose aim is to accurately model the effects of fluctuations in the velocity field on the apparent viscosity within the flowfield. However, velocity is not the only variable to fluctuate due to turbulence and thus numerous researchers have led efforts into the direct modelling of other fluctuating flowfield variables.

Work done by Nagano and Kim [1] introduces a two equation turbulent thermal field model. Sommer, So, and Lai [2], So and Sommer [3], and Sommer, So, and Zhang [4],[5] build on this work by modifying the turbulent thermal field equations to include the effects of viscosity and compressibility while modifying the near wall treatment to obtain behaviour consistent with the physics of the flow. This results in a numerical method that is able to calculate the turbulent Prandtl number directly without a need to set it a priori, allowing a more accurate simulation of flows in which this number can vary significantly within the flowfield (like rocket plumes or scramjet combustors).

For multi-species flows turbulence can increase the apparent mass diffusivity (just as it does for both viscosity and thermal diffusivity) which has led to the development of variable Schmidt number numerical solvers. Brinkman et al. [6] consider non-reacting flows and propose that the turbulent Schmidt number can be calculated directly from the solution of an equation governing the sum of the square of the fluctuations in the species mass fractions and another governing the rate of this quantities' dissipation. This approach is further expanded by Brinkman et al. [7] [8] and Calhoon et al. [9] where the consideration of reacting flows is included (while also replacing the thermal variance equation with one for the internal energy variance). In each of these cases these variable Schmidt number models are coupled to a two equation $k - \omega$ turbulence model. It is interesting to note that in these works even though chemical reactions are considered, the need to model chemical reaction source terms is avoided through the use of two conservation equations, one for the mixture fraction variance and another for the rate of its dissipation.

Although not as common as the two equation $k - \omega$ turbulence model, there has also been development of a variable Schmidt number model with the $k - \zeta$ turbulence model (Robinson and Hassan [10]). This model has been found to work well when using both a variable turbulent Prandtl and Schmidt number approach (Xiao et al. [11][12][13]).

In general, when solving for chemically reacting flows the use of a species massfraction conservation equation leads to the need to model the average of a chemical source term. Terms involving the products of species massfraction fluctuations and the chemical source term appear in other equations as well and thus require additional modelling. A popular approach in handling these terms has been through the use of probability density functions,

or PDFs. Two popular approaches for this method have been to use either an assumed form for the PDF, or to calculate the evolution of the PDF as part of the solution. The evolution approach is based of the work of Pope [14], [15] where the evolution of a joint velocity/composition PDF is solved using a Monte Carlo approach. The advantage of this method is that the effects of convection, reaction, body forces, and the mean pressure gradient appear directly in the equations and thus do not require modelling. However, due to the large dimensionality of the joint PDF this method is computationally expensive and thus many researchers have focused on using an assumed form for the PDF based on the work of Girimaji [16], [17] called the multivariate β PDF.

When comparing the two methods both have been found to produce similar results for the mean flow variables, however, the evolution PDF methods require a significant increase in computational requirements (Calhoon and Kenzakowski [18], Baurle et al. [19] [20] [21]). In all these cases the temperature fluctuations are modelled using an assumed Gaussian distribution (or assumed β function for Calhoon and Kenzakowski) while the massfraction fluctuations are modelled using the assumed multivariate β PDF of Girimaji. The assumed multivariate β PDF approach has difficulty calculating higher order terms due to its assumption of statistical independence between the temperature and the composition. It is also fairly dissipative in the presence of combustion (Keistler et al. [22]) making it less accurate downstream of ignition, but reasonably accurate preceding ignition. It has been shown to be fairly insensitive to the choice of turbulence model in terms of its effect on the calculation of the turbulent mass diffusivity and requires no additional variables to be solved. The requirement of no additional unknown terms other than those already present in most variable Schmidt number solvers makes the assumed multivariate β PDF an attractive choice for many computational codes. Due to the temperature/composition de-coupling it is also possible to treat the fluctuations in temperature and composition differently.

Narayan and Girimaji [23] use an assumed form multivariate β PDF to model massfraction fluctuations while avoiding a PDF for temperature through the use of a series expansion for the reaction rates based on the mean temperature. Alternatively, Gaffney et al. [24] ignore the effect of massfraction fluctuations and model temperature fluctuations as following either an assumed Gaussian or assumed β PDF. They show that temperature fluctuations can have a significant impact on the calculation of reaction rates, while the use of a Gaussian PDF can be sensitive to the clipping limits used (since the exact Gaussian PDF has limits of $\pm\infty$). In addition, Gaffney et al. [25] have studied series expansion for the fluctuations in composition with assumed PDFs for temperature resulting in a method that does not require any numerical integration. Tested on a high speed turbulent reacting hydrogen/air mixing layer (two dimensional) they show that species fluctuations can also have a noticeable effect on the chemical reaction rates.

The multivariate β distribution of Girimaji for the species massfraction PDF has also been tested with various assumed temperature PDFs by Gerlinger [26]. The shape of the assumed temperature PDF (Gaussian, triangular, rectangular) is found to have little effect on the re-

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sults of a supersonic diffusion flame. However, the choice of variance equation from which the temperature fluctuations are extracted shows that a semi-empirical equation achieves the best results (where transport equations for the variance of sensible energy, energy, and temperature are compared).

2 Turbulent, Reacting Flow

For a system in which the fluid composition can change due to chemical reactions, it is often convenient to model a conservation equation for each of the possible species,

$$\frac{\partial}{\partial t}(\rho Y_m) + \frac{\partial}{\partial x_j}(\rho u_j Y_m) - \frac{\partial}{\partial x_j}\left(\rho D_m \frac{\partial Y_m}{\partial x_j}\right) - \dot{\omega}_m = 0 \tag{1}$$

where Y_m is the massfraction of species m,

$$Y_m = \rho_m / \rho \tag{2}$$

Although accurate for laminar flows, Eq. 1 does not account for the fact that under turbulent conditions each of the variables may fluctuate at a given point and thus under these circumstances an average over time can be taken,

$$\overline{\frac{\partial}{\partial t}(\rho Y_m)} + \overline{\frac{\partial}{\partial x_j}(\rho u_j Y_m)} - \overline{\frac{\partial}{\partial x_j}\left(\rho D_m \frac{\partial Y_m}{\partial x_j}\right)} - \overline{\dot{\omega}_m} = 0 \tag{3}$$

where the averaging process indicated by the overline is often referred to as the Reynolds average. For a given variable ϕ,

$$\overline{\phi} = \frac{1}{T}\int_{t=0}^{t=T}\phi \, dt \tag{4}$$

It is also possible to define a density weighted average (often referred to as a Favre average) as,

$$\tilde{\phi} = \frac{1}{\overline{\rho}T}\int_{t=0}^{t=T}\rho\phi \, dt = \frac{\overline{\rho\phi}}{\overline{\rho}} \tag{5}$$

where it is possible to relate several Reynolds and Favre averaged quantities through,

$$\overline{\rho}\tilde{\phi} = \overline{\rho\phi} \tag{6}$$

and

$$\overline{\rho\phi_1\phi_2} = \overline{\rho}\tilde{\phi}_1\tilde{\phi}_2 + \overline{\rho\phi_1''\phi_2''} \tag{7}$$

Therefore, if one assumes a variable can be represented by its Favre averaged value and a fluctuation about this value, then using species massfraction as an example,

$$Y_m = \tilde{Y}_m + Y_m''$$

and Eq. 3 can be expressed as,

$$\frac{\partial}{\partial t}\left(\overline{\rho}\tilde{Y}_m\right) + \frac{\partial}{\partial x_j}\left(\overline{\rho}\tilde{u}_j\tilde{Y}_m\right) + \frac{\partial}{\partial x_j}\left(\overline{\rho}\tilde{D}_m\frac{\partial \tilde{Y}_m}{\partial x_j} - \overline{\rho u_j''Y_m''}\right) - \overline{\dot{\omega}_m} = 0 \tag{8}$$

In obtaining this expression it has been assumed that the dominant effect of turbulence on the mass transfer process is from the large scale movement of turbulent eddies (thus allowing one to assume the effects of u_j'' to be much greater than those due to D_m''). In this form the solution becomes one of finding the time averaged values of quantities such as velocity, species massfraction, and density. However, this inclusion of turbulence now involves the solution of an additional term involving the fluctuating components of both velocity and massfraction, as well as a time averaged value of the species production $\dot{\omega}_m$.

Most numerical models employ the assumption of a turbulent diffusivity, $(\nu_m)_T = \overline{\rho}(D_m)_T$, which is used to approximate the fluctuating terms through,

$$-\overline{\rho u_j''Y_m''} = \overline{\rho}(D_m)_T\frac{\partial \tilde{Y}_m}{\partial x_j} \tag{9}$$

allowing the species conservation equation to take the form,

$$\frac{\partial}{\partial t}\left(\overline{\rho}\tilde{Y}_m\right) + \frac{\partial}{\partial x_j}\left(\overline{\rho}\tilde{u}_j\tilde{Y}_m\right) + \frac{\partial}{\partial x_j}\left[\overline{\rho}(\tilde{D}_m + (D_m)_T)\frac{\partial \tilde{Y}_m}{\partial x_j}\right] - \overline{\dot{\omega}_m} = 0 \tag{10}$$

The calculation of the turbulent diffusivity is often based off of a knowledge of the turbulent co-efficient of viscosity μ_T. This term accounts for the apparent increase in viscous effects due to the fluctuations in velocity and is used to model the Reynolds stresses which appear in the momentum equations after performing a similar averaging process, i.e.,

$$\overline{\rho u_j''u_i''} \approx -\mu_T\frac{\partial \tilde{u}_i}{\partial x_j} \tag{11}$$

There are numerous approaches to calculating a value for μ_T, many of which involve solving an additional one or two conservation equations for various turbulent quantities. Once

found, if one sets a turbulent Schmidt number a priori then this leads directly to a value for $(D_m)_T$ as,

$$(D_m)_T = \frac{\mu_T}{\rho Sc_T} \tag{12}$$

Although this approach can produce satisfactory results, it is dependent on a knowledge of the correct turbulent Schmidt number to set for the particular flowfield under consideration (and thus must often be tailored for a given simulation). However, it is also possible to directly calculate the turbulent diffusivity in a manner similar to that done for the turbulent co-efficient of viscosity through the solution of additional conservation equations. In either case, the sole remaining task for the solution of Eq. 10 is some means of finding the averaged value of the species production terms.

2.1 Expected Value

In the previous section the assumption of a time average is used to postulate the existence of a value that, given a large enough time, will be consistently measured for a given set of circumstances (i.e., initial conditions). This implies that despite the random nature of turbulence, the averaged values solved for would not vary significantly between successive repetitions of the same experiment. The variability across successive experiments (each conducted over a given time period) is evaluated by the ensemble average,

$$\langle \phi \rangle_N = \frac{1}{N} \sum_N \phi_N \tag{13}$$

where the number of successive repetitions of the experiment is N. As the number of repetitions increases, the value of the ensemble average tends towards the *mean*, $\langle \phi \rangle$, or the expected value, which is formally defined as,

$$E(\phi) = \langle \phi \rangle = \int_{-\infty}^{\infty} \psi P_\phi(\psi) d\psi \tag{14}$$

In Eq. 14 $P_\phi(\psi)$ is called the probability density function and it represents the probability that the variable ϕ will have a value equal to ψ, where ψ represents all the values possible for the variable ϕ (i.e., all the realizations of ϕ). In the case of a Gaussian random variable (also known as a normally distributed random variable), the probability density function (hereafter referred to as the PDF) has a bell shape defined by,

$$P_\phi(\psi) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{\psi - \langle \phi \rangle}{\sigma}\right)^2} \tag{15}$$

where σ^2 is the standard deviation. Depending of the values of the mean and the standard deviation the resulting curve can be shifted, sharpened/flattened, or both (see Fig. 1)
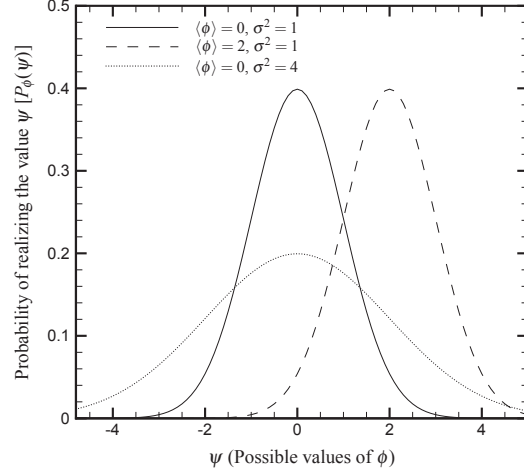

Figure 1: *Gaussian probability distribution function*

If the exact same PDF applies across multiple experiments (i.e., not simply the shape of the PDF but also the mean and standard deviation) then the experiments are said to be statistically stationary (they have the same probability law) and thus from the definitions in Eq. 13 and 14,

$$\langle \phi \rangle_N = \frac{1}{N} [\langle \phi \rangle_1 + \langle \phi \rangle_2 + \cdots + \langle \phi \rangle_N]$$

$$\langle \phi \rangle_N = \frac{1}{N} \left[\int_{-\infty}^{\infty} \psi P_{\phi_1}(\psi) d\psi + \int_{-\infty}^{\infty} \psi P_{\phi_2}(\psi) d\psi + \cdots + \int_{-\infty}^{\infty} \psi P_{\phi_N}(\psi) d\psi \right]$$

but since $P_{\phi_1}(\psi) = P_{\phi_2}(\psi) = P_{\phi_N}(\psi)$ this becomes,

$$\langle \phi \rangle_N = \frac{1}{N} \left[N \int_{-\infty}^{\infty} \psi P_{\phi}(\psi) d\psi \right] = \langle \phi \rangle \tag{16}$$

for all values of N, including $N = 1$. Thus for statistically stationary flows the ensemble average is exactly equal to the mathematical expectation even for a single set of experimental results.

If one postulates that as the time interval over which an average is taken increases (larger T), the difference between values obtained (as defined by Eqs. 4 or 5) will become smaller

between successive repetitions of a given experiment, then the time averaged value ($\tilde{\phi}$) approaches the ensemble average ($\langle\phi\rangle_N$). If the flow is further assumed statistically stationary then by virtue of Eq. 16 this means that the time averaged value of a given variable approaches the mathematical expectation, or mean, of that variable,

$$\tilde{\phi} = \langle\phi\rangle \tag{17}$$

This result provides an interesting approach to finding the time averaged value of any variable (including the time average of a fluctuating variable) through the use of PDFs. Before examining this approach in detail, it is convenient to define the nth central moment (or the nth moment about the mean) as the expectation,

$$E\left([\psi - \langle\phi\rangle]^n\right) = \int_{-\infty}^{\infty} [\psi - \langle\phi\rangle]^n P_\phi(\psi)d\psi \tag{18}$$

where since the mean lies at the centre of the PDF the first central moment is equal to zero. However, the 2nd central moment (also referred to as the variance) is directly related to the standard deviation, σ_ϕ^2, as the expectation of the square of obtaining a value away from the mean,

$$var(\phi) = \sigma_\phi^2 = E\left([\psi - \langle\phi\rangle]^2\right) = \int_{-\infty}^{\infty} [\psi - \langle\phi\rangle]^2 P_\phi(\psi)d\psi \tag{19}$$

This provides a link between fluctuations about a mean value and the PDF. For any variable composed of a time averaged and fluctuating component, when statistical stationary flow is assumed one can write,

$$\phi = \tilde{\phi} + \phi'' = \langle\phi\rangle + \phi'' \qquad \Rightarrow \phi'' = \phi - \langle\phi\rangle$$

The expected value of this fluctuating quantity squared can thus be expressed as,

$$E\left(\phi''\phi''\right) = E\left([\phi - \langle\phi\rangle]^2\right) \tag{20}$$

where comparing the righthand side of Eq. 20 to Eq. 19 shows that the standard deviation is directly related to fluctuating component of the variable under consideration,

$$E\left(\phi''\phi''\right) = \langle\phi''\phi''\rangle = \sigma_\phi^2 \tag{21}$$

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2.2 Chemical Source Term

The solution to Eq. 10 requires a value for $\overline{\dot{\omega}_m}$, the time averaged rate of production or consumption of species m per unit time ($[(kg/(m^3/s)]$). For laminar flows this rate can be calculated from a knowledge of the forward and backwards reaction rate of a given chemical reaction along with the stoichiometric mol numbers of a given species within that reaction as follows. Using the dissociation of hydrogen through a collision with another molecule (B) as an example,

$$2H + B \rightleftharpoons H_2 + B \tag{22}$$

one can define

$$v_m^r: \quad v_H^{\text{reactant}} = 2 \quad v_{H_2}^{\text{reactant}} = 0 \quad v_B^{\text{reactant}} = 1 \tag{23}$$

and

$$v_m^p: \quad v_H^{\text{product}} = 0 \quad v_{H_2}^{\text{product}} = 2 \quad v_B^{\text{product}} = 1$$

For a molecule that does not undergo a change in quantity through the reaction the difference between $v_m^p - v_m^r$ will always be zero while for one which increases in the forwards direction this difference will yield a positive value (and thus a negative value is obtained for a molecule that decreases in the forwards direction). Therefore, if one assumes an overall reaction rate K such that a positive value indicates the forward direction (from left to right in Eq. 22) then the chemical source term can be expressed as,

$$\dot{\omega}_m = \mathscr{M}_m (v_m^p - v_m^r) K \tag{24}$$

provided the overall reaction rate K has units of $(m^3 s)^{-1}$. This rate is found as the difference between the rate at which the given reaction proceeds in the forwards and backwards. The forward reaction rate can be calculated using a modified Arrhenius equation,

$$k_f = A T^n e^{-E_a / \mathfrak{R} T} \tag{25}$$

and the backwards reaction rate is related to k_f through the equilibrium constant based on concentrations,

$$K_c = \frac{k_f}{k_b} \tag{26}$$

It should be noted here that by definition the equilibrium constant based on concentrations is defined as,

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$$K_c(T) = \frac{\left(\frac{\rho Y_1}{\mathcal{M}_1}\right)^{v_1^p}\left(\frac{\rho Y_2}{\mathcal{M}_2}\right)^{v_2^p}\cdots\left(\frac{\rho Y_m}{\mathcal{M}_m}\right)^{v_m^p}}{\left(\frac{\rho Y_1}{\mathcal{M}_1}\right)^{v_1^r}\left(\frac{\rho Y_2}{\mathcal{M}_2}\right)^{v_2^r}\cdots\left(\frac{\rho Y_m}{\mathcal{M}_m}\right)^{v_m^r}} = \frac{\Pi_m\left(\frac{\rho Y_m}{\mathcal{M}_m}\right)^{v_m^p}}{\Pi_m\left(\frac{\rho Y_m}{\mathcal{M}_m}\right)^{v_m^r}}$$

$$K_c(T) = \Pi_m\left(\frac{\rho Y_m}{\mathcal{M}_m}\right)^{v_m^p - v_m^r} \tag{27}$$

where from Eq. 27 it can be seen that the equilibrium constant will have units of concentration (kmols/m^3) raised to the power of $\sum v_m^p - \sum v_m^r$. This requires that the various terms appearing in Eq. 25 (activation energy E_a (per kmol), the exponent n, and the constant A) which vary depending on the particular molecular reaction being considered ($\Re$ is simply the universal gas constant) be such that they yield a rate (i.e. change per unit time) divided by concentration raised to the power of the sum of the reactant mol numbers, $\sum_m v_m^r$. From Eq. 26 this will yield a backwards reaction rate with units of per unit time and per unit concentration raised to the power of the sum of the product mol numbers ($\sum v_m^p$). Under these circumstances, the overall reaction rate can then be calculated on a simple per unit time basis by a multiplication of the forward rate by the sum of the reactant concentrations (each raised to their stoichiometric mol numbers, see Eq. 23) minus the backwards reaction rate multiplied by the product concentrations (raised to their stoichiometric mol numbers).

$$K = k_f\left[\left(\frac{\rho Y_H}{\mathcal{M}_H}\right)^{v_H^r}\left(\frac{\rho Y_{H_2}}{\mathcal{M}_{H_2}}\right)^{v_{H_2}^r}\left(\frac{\rho Y_B}{\mathcal{M}_B}\right)^{v_B^r}\right] - k_b\left[\left(\frac{\rho Y_H}{\mathcal{M}_H}\right)^{v_H^p}\left(\frac{\rho Y_{H_2}}{\mathcal{M}_{H_2}}\right)^{v_{H_2}^p}\left(\frac{\rho Y_B}{\mathcal{M}_B}\right)^{v_B^p}\right]$$

$$K = k_f\rho^{(v_H^r + v_{H_2}^r + v_B^r)}\left[\left(\frac{Y_H}{\mathcal{M}_H}\right)^{v_H^r}\left(\frac{Y_{H_2}}{\mathcal{M}_{H_2}}\right)^{v_{H_2}^r}\left(\frac{Y_B}{\mathcal{M}_B}\right)^{v_B^r}\right]$$

$$- k_b\rho^{(v_H^p + v_{H_2}^p + v_B^p)}\left[\left(\frac{Y_H}{\mathcal{M}_H}\right)^{v_H^p}\left(\frac{Y_{H_2}}{\mathcal{M}_{H_2}}\right)^{v_{H_2}^p}\left(\frac{Y_B}{\mathcal{M}_B}\right)^{v_B^p}\right]$$

Defining the variables

$$\zeta^r = \sum_m v_m^r \qquad \text{and} \qquad \zeta^p = \sum_m v_m^p \tag{28}$$

allows one to re-express the chemical source term in Eq. 24 as,

$$\dot{\omega}_m = \mathcal{M}_m(v_m^p - v_m^r)\left[k_f\rho^{\zeta^r}\Pi_m\left(\frac{Y_m}{\mathcal{M}_m}\right)^{v_m^r} - k_b\rho^{\zeta^p}\Pi_m\left(\frac{Y_m}{\mathcal{M}_m}\right)^{v_m^p}\right]$$

In the case where there is more than one reaction that involves the species m, the above expression is modified slightly (where the number of possible reactions ranges from 1 to j),

$$\dot{\omega}_m = \mathscr{M}_m \sum_j \left\{ (v^p_{m,j} - v^r_{m,j}) \left[k_{f_j} \rho^{\zeta^r_j} \Pi_m \left(\frac{Y_m}{\mathscr{M}_m} \right)^{v^r_{m,j}} - k_{b_j} \rho^{\zeta^p_j} \Pi_m \left(\frac{Y_m}{\mathscr{M}_m} \right)^{v^p_{m,j}} \right] \right\} \quad (29)$$

as now the stoichiometric mol numbers of species as products and reactants depends on the particular reaction j and thus,

$$\zeta^r_j = \sum_m v^r_{m,j} \qquad \text{and} \qquad \zeta^p_j = \sum_m v^p_{m,j} \quad (30)$$

while the definitions of k_f and k_b are the same as those in Eqs. 25 and 26 (only now specific to reaction j).

With Eq. 29 one is now in a position to take the time average of the chemical source term, where since the molecular weights and the stoichiometric mol numbers are constant results in the following,

$$\overline{\dot{\omega}_m} = \mathscr{M}_m \sum_j \left\{ (v^p_{m,j} - v^r_{m,j}) \left[\overline{k_{f_j} \rho}^{\zeta^r_j} \Pi_m \left(\mathscr{M}_m^{-v^r_{m,j}} \overline{Y_m}^{v^r_{m,j}} \right) - \overline{k_{b_j} \rho}^{\zeta^p_j} \Pi_m \left(\mathscr{M}_m^{-v^p_{m,j}} \overline{Y_m}^{v^p_{m,j}} \right) \right] \right\}$$

In this form the challenge becomes how to properly evaluate the average reaction rates (both forward and backward) along with the fluctuations in species massfraction. For example, including turbulent fluctuations in temperature the forward reaction rate (Eq. 25) yields,

$$\overline{k_{f_j}} = A \overline{(\tilde{T} + T'')^n e^{\frac{-E_a}{\mathfrak{R}(\tilde{T} + T'')}}} \quad (31)$$

where even if $T''/\tilde{T}$ is assumed < 1 thus allowing $(\tilde{T} + T'')$ to be expanded in a series still requires numerous terms to be carried through the calculations to be accurate. Similarly, when including turbulent fluctuations in species massfraction one obtains the terms,

$$\Pi_m \overline{(\tilde{Y}_m + Y''_m)}^{v^r_{m,j}} = \overline{(\tilde{Y}_1 + Y''_1)^{v^r_{1,j}} (\tilde{Y}_2 + Y''_2)^{v^r_{2,j}} \cdots (\tilde{Y}_m + Y''_m)^{v^r_{m,j}}}$$

which results in a large number of fluctuating massfraction products that would require modelling.

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Therefore, in order to avoid these difficulties one can replace the average value for $\overline{k}_f, \overline{k}_b$, and $\overline{Y}_m$ directly with their mean values if one assumes statistically stationary flow (Eq. 17),

$$\overline{\dot{\omega}_m} = \mathscr{M}_m \sum_j \left\{ (v_{m,j}^p - v_{m,j}^r) \left[\langle k_{f_j} \rangle \overline{\rho}^{\zeta_j^r} \Pi_m \left(\mathscr{M}_m^{-v_{m,j}^r} \right) \langle \Pi_m Y_m^{v_{m,j}^r} \rangle - \langle k_{b_j} \rangle \overline{\rho}^{\zeta_j^p} \Pi_m \left(\mathscr{M}_m^{-v_{m,j}^p} \right) \langle \Pi_m Y_m^{v_{m,j}^p} \rangle \right] \right\} \tag{32}$$

It should be noted that in obtaining Eq. 32 it has been assumed that the density and the massfractions are jointly independent (see Gaffney et al. [27]).

2.3 Joint PDFs

When using PDFs to find the mean value of a variable, if the variable is found to depend on more than a single independent quantity then a joint PDF is required. However, this then requires that to evaluate the joint PDF one must be capable of integrating over all the independent quantities. For the case of the chemical source term, the rate at which a given species is produced or consumed depends on both the temperature of the mixture as well as the massfractions of the various species that exist at a given time. This means that a joint PDF of both temperature and composition is required,

$$P_{(\mathscr{T},\mathscr{Y}_1,\dots,\mathscr{Y}_m)}(T,Y_1,\dots,Y_m) \tag{33}$$

As with a single variable PDF, when the integration of the joint PDF is taken over the limits of negative and positive infinity the results is still unity (i.e., considering the entire spectrum of possible values for a given variable, the probability is certain),

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} P_{(\mathscr{T},\mathscr{Y}_1,\dots,\mathscr{Y}_m)}(T,Y_1,\dots,Y_m) dT dY_1 \cdots dY_m = 1 \tag{34}$$

However, if one assumes that the species massfractions are jointly independent of the temperature then the joint PDF can be expressed as a multiplication of two separate PDFs,

$$P_{(\mathscr{T},\mathscr{Y}_1,\dots,\mathscr{Y}_m)}(T,Y_1,\dots,Y_m) = P_{\mathscr{T}}(T) P_{\mathscr{Y}_1,\dots,\mathscr{Y}_m}(Y_1,\dots,Y_m) \tag{35}$$

each of which can be evaluated independently.

2.4 Assumed Temperature PDF

Although the assumption that the temperature and species massfractions are uncorrelated (jointly independent) does not reflect the physics of turbulent combustion, it has been applied successfully to mixing flows and thus extended to flows involving combustion as well. When this is done, the temperature can be assumed to have a randomly distributed profile and thus follow a Gaussian PDF,

$$P_{\mathscr{T}}(T) = \frac{1}{\sqrt{2\pi}\sigma_T} e^{-\frac{1}{2}\left(\frac{T-\langle T\rangle}{\sigma_T}\right)^2} \tag{36}$$

For statistically stationary flows one can replace $\langle T\rangle$ with $\tilde{T}$ while from Eq. 21 the standard deviation of the PDF can be replaced with the average of the square of the fluctuations in temperature,

$$P_{\mathscr{T}}(T) = \frac{1}{\sqrt{2\pi\overline{T''T''}}} e^{-\frac{(T-\tilde{T})^2}{2\overline{T''T''}}} \tag{37}$$

Although the Favre averaged temperature is likely a known variable through the standard solution of the Favre averaged energy equation, the fluctuating temperature is generally not a variable in the solution vector. However, several authors have developed methods to avoid the reliance on a pre-determined value for the turbulent Prandtl number allowing the direct calculation of the turbulent eddy thermal conductivity (κ_T) from a set of equations similar to those used for solving for the turbulent eddy viscosity (μ_T). These methods, often referred to as variable Prandtl number models, generally solve for a variance equation (i.e., the expectation of the square of a fluctuating value) and its dissipation. For use in evaluating the turbulent eddy thermal conductivity the variance of either temperature (Nagano and Kim [1]), specific enthalpy (Xiao et al. [28],[13]), or specific energy (Brinckman et al. [7]) have been modelled. In cases where the temperature variance is not modelled directly it can be recovered by neglecting the effect of turbulent fluctuations on the specific heat allowing one to write,

$$\overline{T''T''} = \left(\sum_m C_{p_m} Y_m\right)\overline{h''h''} \quad \text{or} \quad \overline{T''T''} = \left(\sum_m C_{v_m} Y_m\right)\overline{e''e''} \tag{38}$$

Therefore, most variable Prandtl number approaches will already include sufficient information to completely define the temperature PDF in Eq. 37 and thus the mean value of a given reaction rate (either forward or backward) can be found through,

$$\langle k_{f_j}\rangle = \int_0^\infty k_{f_j} P_{\mathscr{T}}(T) dT \tag{39}$$

Several items should be noted when using Eq. 39. The first is that the limits on the integration no longer extend below zero. Physically this is justified in that the temperature cannot fall below this value, however, a truly Gaussian PDF requires that whatever value is being considered has no limits so that the requirement in Eq. 34 is respected,

$$\int_{-\infty}^{\infty} P_{\mathscr{T}}(T)dT = 1 \tag{40}$$

Furthermore, when numerically integrating Eq. 37 finite limits on both ends must be applied leading to a further clipping of the Gaussian PDF. These limits should be set so as to obtain, as close as possible, the result in Eq. 40 over the range,

$$\int_{T_{min}}^{T_{max}} P_{\mathscr{T}}(T)dT \approx 1 \tag{41}$$

while also respecting the fact that over this range the forward reaction rate must be calculated according to the model constants in Eq. 25 which are valid within a finite range (generally between ~ 300 and ~ 3000 K depending on the model chosen). Thus the final result for the mean reaction rate can be expressed as,

$$\langle k_{f_j} \rangle = \int_{T_{min}}^{T_{max}} \frac{k_{f_j}(T)}{\sqrt{2\pi \overline{T''T''}}} e^{-\frac{(T-\tilde{T})^2}{2\overline{T''T''}}} dT \tag{42}$$

Of course, if the variance is zero then the Gaussian PDF approaches the behaviour of a delta function centred at the mean which can cause difficulties for numerical integration. However, as the variance approaches zero this means that the turbulent fluctuations are approaching zero and thus the flow can be treated as laminar, in which case the reaction rate calculated directly from Eq. 25 can be used with $\tilde{T} = T$.

2.5 Assumed Massfraction PDF

To determine the mean value of the massfraction terms in Eq. 32 using a PDF approach one can write

$$\langle \Pi_m Y_m^{\nu_{m,j}} \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(\Pi_m Y_m^{\nu_{m,j}} \right) P_{(\mathscr{Y}_1, \mathscr{Y}_2, \ldots, \mathscr{Y}_m)}(Y_1, Y_2, \ldots, Y_m) dY_1, dY_2, \cdots, dY_m \tag{43}$$

for either the products or the reactants. As the massfractions are raised to the power of the stoichiometric mol numbers of products and reactants Eq. 43 represents moments of the

massfraction PDF. Since the massfraction PDF depends jointly on all the massfractions, i.e., the massfractions cannot be treated as mutually independent,

$$P_{(\mathscr{Y}_1,\mathscr{Y}_2,\ldots,\mathscr{Y}_m)}(Y_1,Y_2,\ldots,Y_m) \neq P_{\mathscr{Y}_1}(Y_1)P_{\mathscr{Y}_2}(Y_2)\cdots P_{\mathscr{Y}_m}(Y_m) \tag{44}$$

this makes the numerical integration of even an assumed Gaussian PDF difficult. Therefore, Girimaji [16] proposed the use of a multivariate β distribution defined as,

$$P_{(\mathscr{Y}_1,\mathscr{Y}_2,\ldots,\mathscr{Y}_m)}(Y_1,Y_2,\ldots,Y_m) = \frac{\Gamma(\beta_1+\beta_2+\ldots+\beta_m)}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)}\left\{Y_1^{\beta_1-1}Y_2^{\beta_2-1}\cdots Y_m^{\beta_m-1}\delta\left(1-[Y_1-Y_2-\ldots-Y_m]\right)\right\} \tag{45}$$

where δ is the Dirac delta function and the variable $\beta = f(\tilde{Y}_m, \overline{Y_m''Y_m''})$ and is defined as,

$$\beta_m = \tilde{Y}_m\left\{\frac{1-\Sigma\tilde{Y}_m^2}{\Sigma\overline{Y_m''Y_m''}}-1\right\} \tag{46}$$

As with the assumed temperature PDF, this assumed massfraction PDF requires a knowledge of both the average massfraction value and a value for its variance. Most numerical models that consider more than a single composition fluid will have a species conservation equation similar to Eq. 10 and so $\tilde{Y}_m$ will be known. The sum of the square of the fluctuations in the species massfractions (sometimes referred to as the turbulent scalar energy) is not typically a value that is solved for. However, development of variable Schmidt number codes (see Baurle et al. [19]) often solve for this value (and the rate of its dissipation) as a consequence of avoiding the pre-specification of a turbulent Schmidt number to determine the turbulent mass diffusivity $(D_m)_T$. In general the form of the massfraction variance equation can be expressed as,

$$\frac{\partial}{\partial t}(\overline{\rho}\sigma_Y) + \frac{\partial}{\partial x_j}(\overline{\rho}\tilde{u}_j\sigma_Y) = \frac{\partial}{\partial x_j}\left(\overline{\rho}[D_m+C_{Y1}(D_m)_T]\frac{\partial\sigma_Y}{\partial x_j}\right)$$
$$+2\Sigma_m\left(\overline{\rho}(D_m)_T\left(\frac{\partial\tilde{Y}_m}{\partial x_j}\right)^2-\overline{\rho}\varepsilon_Y+\overline{Y_m''\dot{\omega}_m}\right) \tag{47}$$

where

$$\sigma_Y = \sum_m \overline{Y_m''Y_m''} \tag{48}$$

Along with the solution of Eq. 47, most variable Schmidt number models solve for a similar equation for the dissipation rate of σ_Y, or ε_Y, to close the set of equations.

With both the averaged value of massfraction and its variance solved for, β_m is completely determined and so returning to Eq. 43 and substituting the multivariate β PDF in Eq. 45 for $P_{(\mathscr{Y}_1,\mathscr{Y}_2,\ldots,\mathscr{Y}_m)}(Y_1,Y_2,\ldots,Y_m)$ yields

$$\left\langle Y_1{}^{v_{1,j}}Y_2{}^{v_{2,j}}\cdots Y_m{}^{v_{m,j}}\right\rangle = \frac{\Gamma(\beta_1+\beta_2+\ldots+\beta_m)}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)}$$

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\left(Y_1{}^{v_{1,j}}Y_2{}^{v_{2,j}}\cdots Y_m{}^{v_{m,j}}\right)\left(Y_1^{\beta_1-1}Y_2^{\beta_2-1}\cdots Y_m^{\beta_m-1}\right)\delta\left(1-[Y_1-Y_2-\ldots-Y_m]\right)dY_1,dY_2,\ldots,dY_m$$

$$\left\langle Y_1{}^{v_{1,j}}Y_2{}^{v_{2,j}}\cdots Y_m{}^{v_{m,j}}\right\rangle = \frac{\Gamma(\beta_1+\beta_2+\ldots+\beta_m)}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)}$$

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\left(Y_1{}^{\alpha_1}Y_2{}^{\alpha_2}\cdots Y_m{}^{\alpha_m}\right)\delta\left(1-[Y_1-Y_2-\ldots-Y_m]\right)dY_1,dY_2,\ldots,dY_m \tag{49}$$

where

$$\alpha_m = v_{m,j}+\beta_m-1 = \theta_m-1 \tag{50}$$

Examining only the integral, if one performs the integration with respect to Y_m first,

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}Y_1{}^{\alpha_1}\cdots Y_{m-1}^{\alpha_{m-1}}\left\{\int_{-\infty}^{\infty}Y_m{}^{\alpha_m}\delta\left(1-[Y_1-\ldots-Y_{m-1}]-Y_m\right)dY_m\right\}dY_1,\ldots,dY_{m-1}$$

Noting that the only time the Dirac delta function is non zero is when its argument is zero one can define,

$$Y_m^* = 1-(Y_1+\cdots+Y_{m-1})$$

while noting that $\delta(-x) = \delta(x)$ (i.e., the delta function is an even function) and that by virtue of its sifting property one can write,

$$\int_{-\infty}^{\infty}g(y)\delta(y-c) = g(c) \tag{51}$$

then letting $g(y) = g(Y_m) = Y_m^{\alpha_m}$ and $\delta(y-c) = \delta(Y_m-Y_m^*)$ one obtains,

$$\int_{-\infty}^{\infty}Y_m{}^{\alpha_m}\delta\left(1-[Y_1-\ldots-Y_{m-1}]-Y_m\right)dY_m = (Y_m^*)^{\alpha_m} = (1-Y_1-\cdots-Y_{m-1})^{\alpha_m}$$

and thus one is left with

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$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} Y_1^{\alpha_1} \cdots Y_{m-1}^{\alpha_{m-1}} (1 - Y_1 - \cdots - Y_{m-1})^{\alpha_m} dY_1, \ldots, dY_{m-1} \tag{52}$$

If one defines,

$$Y_m^{**} = 1 - Y_1 - Y_2 - \cdots - Y_{m-2}$$

then the integral with respect to Y_{m-1} can be written,

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} Y_1^{\alpha_1} \cdots Y_{m-2}^{\alpha_{m-2}} \underbrace{\left\{ \int_{-\infty}^{\infty} Y_{m-1}^{\alpha_{m-1}} (Y_m^{**} - Y_{m-1})^{\alpha_m} dY_{m-1} \right\}}_{} dY_1, \ldots, dY_{m-2} \tag{53}$$

$$\overbrace{\int_{-\infty}^{\infty} Y_{m-1}^{\alpha_{m-1}} \left(\frac{Y_m^{**}}{Y_m^{**}} \right)^{\alpha_m} (Y_m^{**} - Y_{m-1})^{\alpha_m} dY_{m-1} = (Y_m^{**})^{\alpha_m} \int_{-\infty}^{\infty} Y_{m-1}^{\alpha_{m-1}} (1 - \frac{Y_{m-1}}{Y_m^{**}})^{\alpha_m} dY_{m-1}}$$

Noting that the sum off all the massfractions must equal unity allows one to rephrase the above integral by observing that,

$$Y_1 + Y_2 + \cdots + Y_{m-2} + Y_{m-1} + Y_m = 1$$

$$Y_{m-1} + Y_m = 1 - (Y_1 + Y_2 + \cdots + Y_{m-2})$$

and thus one can change the variable of integration using the relations,

$$x = \frac{Y_{m-1}}{Y_m^{**}} = \frac{Y_{m-1}}{1 - Y_1 - Y_2 - \cdots - Y_{m-2}} = \frac{Y_{m-1}}{Y_{m-1} + Y_m} \tag{54}$$

and

$$dY_{m-1} = Y_m^{**} dx \tag{55}$$

When there is no species Y_{m-1} then $x = 0$ while in the case where the entire mixture is simply species Y_{m-1} then it must be that $Y_m = 0$ and thus $x = 1$. Therefore, using the new

variable of integration in Eq. 54 and applying the new limits yields for the integration with respect to Y_{m-1},

$$(Y_m^{**})^{\alpha_m} \int_0^1 \{x Y_m^{**}\}^{\alpha_{m-1}} (1-x)^{\alpha_m} \{Y_m^{**} dx\} = (Y_m^{**})^{1+\alpha_m+\alpha_{m-1}} \int_0^1 x^{\alpha_{m-1}} (1-x)^{\alpha_m} dx$$

and so the integral with respect to Y_{m-1} can be written,

$$\int_{-\infty}^{\infty} Y_{m-1}^{\alpha_{m-1}} (Y_m^{**} - Y_{m-1})^{\alpha_m} dY_{m-1} = (Y_m^{**})^{1+\theta_m-1+\theta_{m-1}-1} \int_0^1 x^{\theta_{m-1}-1} (1-x)^{\theta_m-1} dx \quad (56)$$

At this point one of the first advantages of using the assumed PDF form as presented in Eq. 45 presents itself in that the remaining integral is by definition the beta function which itself can be expressed as a function of several gamma functions,

$$\int_0^1 x^{t_1-1}(1-x)^{t_2-1} dx = \frac{\Gamma(t_1)\Gamma(t_2)}{\Gamma(t_1+t_2)} \quad (57)$$

Combining the results of Eqs. 57 and 56 allows the integral portion of Eq. 49 to be expressed as (while also using the relation in Eq. 50),

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (Y_1^{\alpha_1} Y_2^{\alpha_2} \cdots Y_m^{\alpha_m}) \, \delta \left(1 - [Y_1 - Y_2 - \ldots - Y_m]\right) dY_1, dY_2, \ldots, dY_m =$$

$$\frac{\Gamma(\theta_m)\Gamma(\theta_{m-1})}{\Gamma(\theta_m+\theta_{m-1})} \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_1^{\theta_1-1} \cdots Y_{m-2}^{\theta_{m-2}-1}\right) (1 - Y_1 - Y_2 - \cdots - Y_{m-2})^{\theta_m+\theta_{m-1}-1} dY_1, \ldots, dY_{m-2}}$$

$$(58)$$

The integral in the above expression has a form similar to that in Eq. 52 except that the outer two integrations have been performed. If one defines,

$$\gamma_m = \theta_m + \theta_{m-1} \quad (59)$$

and

$$Y_m^{***} = 1 - Y_1 - Y_2 - \cdots Y_{m-3}$$

then Eq. 58 can be expressed as,

$$\frac{\Gamma(\theta_m)\Gamma(\theta_{m-1})}{\Gamma(\theta_m+\theta_{m-1})} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_1^{\theta_1-1} \cdots Y_{m-2}^{\theta_{m-2}-1}\right) (Y_m^{***} - Y_{m-2})^{\gamma_m-1} dY_1, \ldots, dY_{m-2}$$

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and thus the integration with respect to Y_{m-2} can be isolated,

$$\frac{\Gamma(\theta_m)\Gamma(\theta_{m-1})}{\Gamma(\theta_m+\theta_{m-1})} \int_{-\infty}^{\infty} \left(Y_1{}^{\theta_1-1}\cdots Y_{m-3}^{\theta_{m-3}-1}\right) \left\{\int_{-\infty}^{\infty} Y_{m-2}^{\theta_{m-2}-1} \left(Y_m^{***}-Y_{m-2}\right)^{\gamma_m-1} dY_{m-2}\right\} dY_1,\ldots,dY_{m-3}$$

(60)

and evaluated in a similar manner to that in Eq. 53,

$$\int_{-\infty}^{\infty} Y_{m-2}^{\theta_{m-2}-1} \left(\frac{Y_m^{***}}{Y_m^{***}}\right)^{\gamma_m-1} \left(Y_m^{***}-Y_{m-2}\right)^{\gamma_m-1} dY_{m-2}$$

$$(Y_m^{***})^{\gamma_m-1} \int_{-\infty}^{\infty} Y_{m-2}^{\theta_{m-2}-1} \left(1-\frac{Y_{m-2}}{Y_m^{***}}\right)^{\gamma_m-1} dY_{m-2}$$

Noting that

$$Y_1+Y_2+\cdots Y_{m-3}+Y_{m-2}+Y_{m-1}+Y_m = 1 = Y_m^{***}+Y_{m-2}+Y_{m-1}+Y_m$$

thus

$$1-Y_m^{***} = Y_{m-2}+Y_{m-1}+Y_m$$

allowing one to again change the variable of integration by defining,

$$x = \frac{Y_{m-2}}{Y_m^{***}} = \frac{Y_{m-2}}{Y_{m-2}+Y_{m-1}+Y_m} \quad \text{and} \quad dY_{m-2} = Y_m^{***}dx$$

where as before when there is no species Y_{m-2} then $x=0$ while if the entire mixture is pure Y_{m-2} then all remaining massfractions must be zero and thus $x=1$. With this change the integral becomes,

$$(Y_m^{***})^{\gamma_m-1} \int_0^1 \{Y_m^{***}x\}^{\theta_{m-2}-1} (1-x)^{\gamma_m-1} \{Y_m^{***}dx\}$$

$$(Y_m^{***})^{\gamma_m-1+\theta_{m-2}-1+1} \int_0^1 x^{\theta_{m-2}-1} (1-x)^{\gamma_m-1} dx = (Y_m^{***})^{(\gamma_m+\theta_{m-2}-1)} \frac{\Gamma(\theta_{m-2})\Gamma(\gamma_m)}{\Gamma(\theta_{m-2}+\gamma_m)}$$

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where the definition of the beta function in Eq. 57 has been applied. Replacing the holders γ_m and Y_m^{***} yields for the integral with respect to Y_{m-2},

$$\int_{-\infty}^{\infty} Y_{m-2}^{\theta_{m-2}-1} \left(Y_m^{***} - Y_{m-2}\right)^{\gamma_m-1} dY_{m-2} = (1 - Y_1 - Y_2 - \cdots Y_{m-3})^{(\theta_{m-2}+\theta_{m-1}+\theta_m-1)} \frac{\Gamma(\theta_{m-2})\Gamma(\theta_m+\theta_{m-1})}{\Gamma(\theta_{m-2}+\theta_{m-1}+\theta_m)}$$

(61)

When this results is substituted back into Eq. 60 the result becomes,

$$\frac{\Gamma(\theta_m)\Gamma(\theta_{m-1})}{\Gamma(\theta_m+\theta_{m-1})} \frac{\Gamma(\theta_{m-2})\Gamma(\theta_m+\theta_{m-1})}{\Gamma(\theta_{m-2}+\theta_{m-1}+\theta_m)}$$

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_1^{\theta_1-1} \cdots Y_{m-3}^{\theta_{m-3}-1}\right)(1 - Y_1 - Y_2 - \cdots Y_{m-3})^{(\theta_{m-2}+\theta_{m-1}+\theta_m-1)} dY_1, \ldots, dY_{m-3}$$

(62)

Cancelling like terms it can now be noted that the integrals in Eq. 58 and 62 have the identical form but for the reduction in the variables of integration by one. Therefore, the process outlined between Eqs. 60 and Eq. 62 can be repeated until all the integrations have been performed yielding the final result for the integral in Eq. 49 (replacing the holder θ_m),

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_1^{v_{1,j}} Y_2^{v_{2,j}} \cdots Y_m^{v_{m,j}}\right) \left(Y_1^{\beta_1-1} Y_2^{\beta_2-1} \cdots Y_m^{\beta_m-1}\right) \delta\left(1 - [Y_1 - Y_2 - \ldots - Y_m]\right) dY_1, dY_2, \ldots, dY_m$$

$$= \frac{\Gamma(v_{1,j}+\beta_1)\Gamma(v_{2,j}+\beta_2) \cdots \Gamma(v_{m,j}+\beta_m)}{\Gamma(\beta_1+\beta_2+\cdots+\beta_m+v_{1,j}+v_{2,j}+\cdots+v_{m,j})}$$

(63)

With this integral evaluated, the mean value of the massfraction terms appearing in Eq. 32 can be re-expressed by combining Eq. 63 with Eq. 49 to obtain the final result,

$$\langle \Pi_m Y_m^{v_{m,j}} \rangle = \frac{\Gamma(\beta_1+\beta_2+\ldots+\beta_m)}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)} \frac{\Gamma(v_{1,j}+\beta_1)\Gamma(v_{2,j}+\beta_2)\cdots\Gamma(v_{m,j}+\beta_m)}{\Gamma(\beta_1+\beta_2+\cdots+\beta_m+v_{1,j}+v_{2,j}+\cdots+v_{m,j})} \quad (64)$$

It is at this point that the second benefit of using the assumed form of the PDF in Eq. 45 becomes apparent. Since the gamma function $\Gamma(\beta)$ itself has the definition,

$$\Gamma(t) = \int_0^1 x^{t-1} e^{-x} dx \quad (65)$$

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one can make use of the fact that for positive integer values an equivalent definition of this function is,

$$\Gamma(t) = (t-1)! = (1)(2)\cdots(t-1) \tag{66}$$

and thus one can write,

$$\Gamma(t+1) = (1)(2)\cdots([t+1]-2)([t+1]-1) = (1)(2)\cdots(t-1)t = t\,[(t-1)!]$$

leading to the identity,

$$\Gamma(t+1) = t\Gamma(t) \tag{67}$$

Repeated use of this identity allows the gamma functions in Eq. 64 to be continually reduced since $v_{m,j}$ is an integer value,

$$
\begin{aligned}
\Gamma(\beta_m + v_{m,j}) &= (\beta_m + v_{m,j} - 1)\underbrace{\Gamma(\beta_m + v_{m,j} - 1)} \\
&= (\beta_m + v_{m,j} - 1)\overbrace{(\beta_m + v_{m,j} - 2)\underbrace{\Gamma(\beta_m + v_{m,j} - 2)}} \\
&= (\beta_m + v_{m,j} - 1)(\beta_m + v_{m,j} - 2)\overbrace{(\beta_m + v_{m,j} - 3)\Gamma(\beta_m + v_{m,j} - 3)}
\end{aligned}
$$

Therefore,

$$\Gamma(\beta_m + v_{m,j}) = \Gamma(\beta_m)\Pi_{i=1}^{i=v_{m,j}}(\beta_m + v_{m,j} - i) \tag{68}$$

Similarly,

$$\Gamma(\sum_m \beta_m + \sum_m v_{m,j}) = \Gamma(\sum_m \beta_m)\Pi_{k=1}^{k=\sum_m v_{m,j}}(\sum_m \beta_m + \sum_m v_{m,j} - k) \tag{69}$$

Therefore, as these two terms appear as a ratio in Eq. 64 one can write,

$$\langle \Pi_m Y_m{}^{v_{m,j}} \rangle =$$

$$\frac{\Gamma(\sum_m \beta_m)\left\{\Gamma(\beta_1)\Pi_{i=1}^{i=v_{1,j}}(\beta_1 + v_{1,j} - i)\right\}\left\{\Gamma(\beta_2)\Pi_{i=1}^{i=v_{2,j}}(\beta_2 + v_{2,j} - i)\right\}\cdots\left\{\Gamma(\beta_m)\Pi_{i=1}^{i=v_{m,j}}(\beta_m + v_{m,j} - i)\right\}}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)\Gamma(\sum_m \beta_m)\Pi_{k=1}^{k=\sum_m v_{m,j}}(\sum_m \beta_m + \sum_m v_{m,j} - k)}$$

where after cancelling all the like terms reduces to the simple algebraic expression,

$$\langle \Pi_m Y_m^{v_{m,j}} \rangle = \frac{\left\{ \Pi_{i=1}^{i=v_{1,j}} (\beta_1 + v_{1,j} - i) \right\} \left\{ \Pi_{i=1}^{i=v_{2,j}} (\beta_2 + v_{2,j} - i) \right\} \cdots \left\{ \Pi_{i=1}^{i=v_{m,j}} (\beta_m + v_{m,j} - i) \right\}}{\Pi_{k=1}^{k=\Sigma_m v_{m,j}} (\Sigma_m \beta_m + \Sigma_m v_{m,j} - k)}$$

(70)

where this expression applies equally to both the product and reactant terms. It is interesting to note that the solution for the mean value of the terms when using the assumed multivariate β PDF form in Eq. 45 does not actually require the solution to the PDF directly. This is in contrast to that for the temperature, where although assuming a seemingly more intuitive Gaussian PDF, its solution requires integration as shown in Eq. 42. To use Eq. 70 all that is required is the mean value of the species massfraction and its variance (Eq. 48), both of which can be found from conservation equations likely to already exist in a variable Schmidt number solver.

As a final consideration it should be noted that in the species massfraction variance equation (Eq. 47) the term $\overline{Y_m'' \dot{\omega}_m}$ appears. Re-expressing the species massfraction as the sum of its Favre average and fluctuating components,

$$\sum_m \overline{Y_m \dot{\omega}_m} = \sum_m \overline{(\tilde{Y}_m + Y_m'') \dot{\omega}_m} = \sum_m \left(\tilde{Y}_m \overline{\dot{\omega}_m} + \overline{Y_m'' \dot{\omega}_m} \right)$$

this can be re-arranged to yield,

$$\sum_m \overline{Y_m'' \dot{\omega}_m} = \underbrace{\sum_m \tilde{Y}_m \overline{\dot{\omega}_m}}_{A} - \underbrace{\sum_m \overline{Y_m \dot{\omega}_m}}_{B}$$

(71)

Term A simply requires the mean value for the chemical source term which has already been found through the procedure outlined. For the second term (B) using the expression for the chemical source term in Eq. 32 one can write,

$$\overline{Y_m \dot{\omega}_m} = \overline{Y_\xi \dot{\omega}_\xi} =$$

$$\mathcal{M}_\xi \sum_j \left\{ (v_{\xi,j}^p - v_{\xi,j}^r) \left[\langle k_{f_j} \rangle \overline{\rho}^{\zeta_j^r} \Pi_m \left(\mathcal{M}_m^{-v_{m,j}^r} \right) \langle Y_\xi \Pi_m Y_m^{v_{m,j}^r} \rangle - \langle k_{b_j} \rangle \overline{\rho}^{\zeta_j^p} \Pi_m \left(\mathcal{M}_m^{-v_{m,j}^p} \right) \langle Y_\xi \Pi_m Y_m^{v_{m,j}^p} \rangle \right] \right\}$$

(72)

where again the time averaged massfraction terms have been replaced with the expected, or mean values. Using the same assumed form for the massfraction PDF, the means appearing in Eq. 72 are simply moments of this PDF and thus can be computed in the same

fashion as done for the means appearing in Eq. 32. In this case the moment being sought is,

$$\langle Y_\xi \Pi_m Y_m{}^{v_{m,j}} \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_\xi \Pi_m Y_m{}^{v_{m,j}} \right) P_{(\mathscr{Y}_1, \mathscr{Y}_2, \ldots, \mathscr{Y}_m)}(Y_1, Y_2, \ldots, Y_m) dY_1, dY_2, \cdots, dY_m$$
(73)

where after substituting the assumed form for the PDF in Eq. 45 yields,

$$\langle Y_\xi Y_1{}^{v_{1,j}} Y_2{}^{v_{2,j}} \cdots Y_m{}^{v_{m,j}} \rangle = \frac{\Gamma(\beta_1 + \beta_2 + \ldots + \beta_m)}{\Gamma(\beta_1)\Gamma(\beta_2)\cdots\Gamma(\beta_m)}$$
(74)

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(Y_\xi Y_1{}^{\alpha_1} Y_2{}^{\alpha_2} \cdots Y_m{}^{\alpha_m} \right) \delta \left(1 - [Y_1 - Y_2 - \ldots - Y_m] \right) dY_1, dY_2, \ldots, dY_m$$

where α_m has the same definition as in Eq. 50. Performing the same steps as outlined from Eq. 49 for all the variables of integration except for dY_ξ will yield the same result as shown in Eq. 62 leaving for the final integration step,

$$\frac{\Gamma(\theta_1)\Gamma(\theta_2)\cdots\Gamma(\theta_{m-1})}{\Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1})} \int_{-\infty}^{\infty} \left(Y_m Y_m{}^{\theta_m - 1} \right) (1 - Y_m)^{(\theta_1 + \theta_2 + \cdots + \theta_{m-1} - 1)} dY_m$$

Defining

$$\xi_m = \theta_1 + \theta_2 + \cdots + \theta_{m-1} \quad \text{and} \quad x = Y_m \quad \text{and thus} \quad dx = dY_m \quad (75)$$

allows the integral to be rephrased as,

$$\frac{\Gamma(\theta_1)\Gamma(\theta_2)\cdots\Gamma(\theta_{m-1})}{\Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1})} \int_0^1 x^{\theta_m} (1 - x)^{(\xi_m - 1)} dx$$

where as before, if the mixture has no Y_m then $x = 0$ while for a mixture of pure Y_m, $x = 1$. Using the result for the beta function (Eq. 57) where in this case $t_1 - 1 = \theta_m$ allows one to replace the integral to obtain,

$$\frac{\Gamma(\theta_1)\Gamma(\theta_2)\cdots\Gamma(\theta_{m-1})}{\Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1})} \frac{\Gamma(\theta_m + 1)\Gamma(\xi_m)}{\Gamma(\theta_m + 1 + \xi_m)}$$

Noting that $\Gamma(\xi_m) = \Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1})$ these terms cancel leaving,

$$\frac{\Gamma(\theta_1)\Gamma(\theta_2)\cdots\Gamma(\theta_{m-1})\Gamma(\theta_m + 1)}{\Gamma(\theta_m + 1 + \xi_m)}$$
(76)

From the identity expressed in Eq. 67 one can write

$$\Gamma(\theta_m + 1) = \theta_m \Gamma(\theta_m)$$

and

$$\Gamma(\xi_m + \theta_m + 1) = \Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1} + \theta_m + 1)$$

$$= (\theta_1 + \theta_2 + \cdots + \theta_{m-1} + \theta_m)\Gamma(\theta_1 + \theta_2 + \cdots + \theta_{m-1} + \theta_m)$$

which allows Eq. 76 to be written,

$$\frac{\theta_m \{\Gamma(\theta_1)\Gamma(\theta_2)\cdots\Gamma(\theta_{m-1})\Gamma(\theta_m)\}}{(\theta_1 + \theta_2 + \cdots + \theta_m)\Gamma(\theta_1 + \theta_2 + \cdots + \theta_m)} \tag{77}$$

This has the exact same form as the result expressed in Eq. 63 but for the additional pre-multiplying term,

$$\frac{\theta_m}{(\theta_1 + \theta_2 + \cdots + \theta_{m-1} + \theta_m)} = \frac{(\nu_{m,j} + \beta_m)}{(\beta_1 + \beta_2 + \cdots + \beta_m + \nu_{1,j} + \nu_{2,j} + \cdots + \nu_{m,j})} \tag{78}$$

and thus application of the results expressed by Eqs. 68 and 69 will yield a final result almost identical to that found in Eq. 70,

$$\langle Y_\xi \Pi_m Y_m^{\nu_{m,j}} \rangle = \left\{ \frac{(\nu_{m,j} + \beta_m)}{(\sum_m \beta_m + \sum_m \nu_{m,j})} \right\}$$

$$\frac{\left\{ \Pi_{i=1}^{i=\nu_{1,j}} (\beta_1 + \nu_{1,j} - i) \right\} \left\{ \Pi_{i=1}^{i=\nu_{2,j}} (\beta_2 + \nu_{2,j} - i) \right\} \cdots \left\{ \Pi_{i=1}^{i=\nu_{m,j}} (\beta_m + \nu_{m,j} - i) \right\}}{\Pi_{k=1}^{k=\sum_m \nu_{m,j}} (\sum_m \beta_m + \sum_m \nu_{m,j} - k)} \tag{79}$$

where again this applies equally to the product and reactant terms appearing in Eq. 72. As with Eq. 70 the solution to the assumed multivariate β PDF is not required to evaluate the mean as expressed in Eq. 79. As before, if one can calculate $\beta = f(\tilde{Y}_m, \sigma_y)$ (Eq. 46) then along with the stoichiometric mol numbers of the reactant and product species involved in a given reaction j, one need only solve an algebraic expression to obtain the time averaged chemical source terms appearing in the species continuity (Eq. 10) and massfraction variance (Eq. 47) equations.

3   Recommendations

Due to its resulting computational simplicity, the use of an assumed multivariate β PDF has been used in a wide variety of flowfields outside the original scope of its original proposed use for turbulent mixing. By assuming statistical independence between the temperature and the massfraction fluctuations, the assumed massfraction PDF matches the behaviour of the real PDF in regions where turbulent mixing alone occurs. It can be shown that the behaviour of this assumed PDF in the limit approaches that of a standardized Gaussian PDF (which matches observed results from Direct Numerical Simulations for two scalar mixing over all stages of the mixing process). However the highly dissipative nature of the term $\overline{Y_m'' \dot{\omega}_m}$ found in the conservation equation for the dissipation of the sum of the massfraction variance causes discrepancies between the model and experiment for regions where chemical reactions are occurring (mean flow properties are reasonably consistent with experiment). This has led recent researchers to simply model these terms to improve comparison with experiment (Keistler, Hassan, and Xiao [29],[30], Keistler and Hassan [31]).

Evolution PDFs, although capable of potentially overcoming some of the issues with the assumed PDF approach by incorporating more variables within a single joint PDF, still require computational resources that make their use prohibitive. However, their strong theoretical basis make them an attractive alternative and thus it is recommended a comprehensive review of evolution PDF methods and their recent application to high speed reacting flows be conducted. Within this review, alternatives to the assumed multivariate β PDF should be examined in an effort to establish if progress has been made to reduce the dissipative effect of certain terms that appear within the variance dissipation equation.

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List of Acronyms and Symbols

Acronyms

PDF   Probability Density Function
DRDC   Defence Research and Development Canada

Greek Symbols

δ Dirac delta function
ε_Y Dissipation of massfraction variance
Γ Gamma function
κ Laminar thermal conductivity
μ Laminar co-efficient of viscosity
ν_m Species mass diffusivity, stoichiometric mole number
ρ Density
σ Standard deviation
σ_Y Sum of mass fraction variances
ω Specific dissipation of k
$\dot{\omega}_m$ Rate of production or consumption of species m
ζ Enstrophy

Roman Symbols

C_p Specific heat at constant pressure
C_v Specific heat at constant volume
D_m Species mass diffusion co-efficient
e Specific energy
E Expectation
E_a Activation energy
h Specific enthalpy
k Specific turbulent kinetic energy
k_b Backward reaction rate

k_f	Forward reaction rate
K	Reaction rate
K_c	Equilibrium constant based on concentrations
$\mathscr{M}_m$	Species molecular weight
N	Number of experiments
P_ϕ	Probability density function of ϕ
$\mathscr{R}$	Universal gas constant
Sc	Schmidt number
t	Time
T	Temperature, time
u	velocity
Y	Mass fraction

Subscripts

m	Species
T	Turbulent

Superscripts

$''$	Favre fluctuating component
p	Product
r	Reactant